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This program has produced detailed information concerning the chemical behavior of halogen isocyanate, halogen amine, and halogen azide systems. These types of molecules can store considerable amounts of energy, which can be released by photolysis, chemical reaction, or energy transfer processes. In a number of the particular cases studied, the energy release was strongly constrained by angular momentum conservation rules. The data obtained from this program are relevant to the development of new laser systems, new propellants, and the understanding of combustion processes.

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I. INTRODUCTION

This report describes research performed during the period 15 April 1987 to 15 April 1990 under the auspices of AFOSR Grant No. AFOSR-87-0210. The program, entitled "Physical Chemistry of Energetic Nitrogen Compounds," had as its global objectives the development of an understanding of energy storage mechanisms in small nitrogen containing molecules, and of the dynamics of dissociation processes, reactions, and energy transfer systems in which these species take part. This information is relevant to a number of specific issues of concern to the scientific community and the DOD, in particular the development of new high energy density propellants, new laser systems, and the modeling of energetic phenomena in the atmosphere.

The program was divided into three general areas of research, which were energetic processes in isocyanate systems, halogen amine chemistry, and dissociation processes in halogen azides. These three areas represent different classes of highly energetic nitrogen-halogen molecular systems which are particularly relevant to the issues noted above. In each area, a number of individual projects were performed. Since the results of these projects have been reported in detail in publications in the open literature (See Section V below), only a brief summary of each project, along with an assessment of the significance of the results, is presented below.

II. ENERGETIC PROCESSES IN ISOCYANATE SYSTEMS

1. Photochemistry of ClNCO

The halogen isocyanates (XNCO, X = halogen) are isoelectronic to the very highly energetic halogen azide molecules, whose photochemistry was studied in our laboratory under a previous AFOSR supported program.[1] The isocyanates are interesting in that they are a much better behaved species (e.g., they can be purified by fractional condensation without exploding[2]), yet are still metastable with respect to dissociation to ground state NX and N_2 fragments.[3] The issues of interest for these molecules are the amounts of energy they contain (i.e., their heats of formation), and the specific mechanisms of energy release upon reaction or photodissociation.

Figure 1 shows UV absorption spectra recorded in our laboratory[4] for ClNCO, BrNCl, and INCO. Three distinct absorptions are evident in each case, with a clear progression to higher wavelengths in the series ClNCO, BrNCO, INCO. Also of interest is the fact that these absorptions are such that wavelengths generated by excimer lasers are readily absorbed. Wavelengths corresponding to ArF, KrCl, KrF, XeCl, and XeF transitions are shown by arrows in the figure. Hence, pulsed photodissociation experiments were conveniently performed by excimer laser photolysis of XNCO/diluent gas mixtures. In each case, the halogen isocyanate was synthesized on-line in our lab as described in the literature.[2,4,5] Similarly, the apparatus for pulsed dissociation, time resolved monitoring of photoproducts by emission, LIF, or other means, and electronics for data handling and manipulation
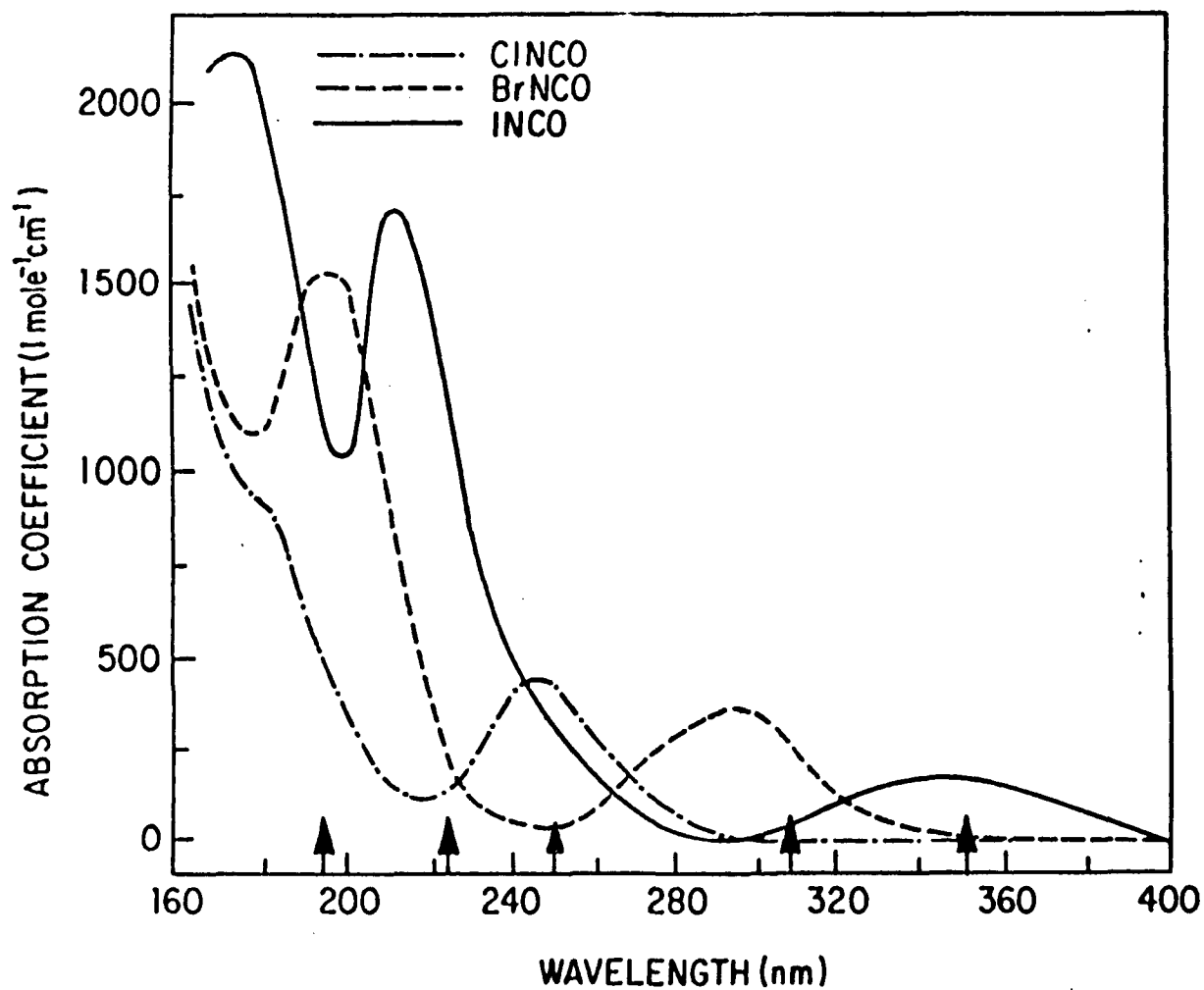
Figure 1. Absorption spectra of gaseous halogen isocyanates. Arrows indicate the wavelengths of excimer laser photolysis sources.
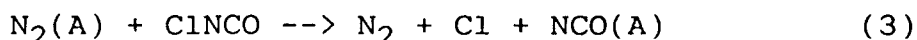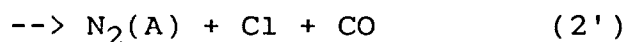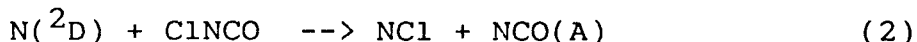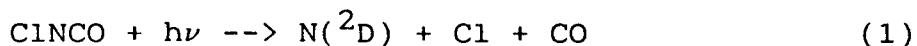
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has been described in a number of publications.[3-5]

An extensive study was made of ClNCO photodissociation at 249 nm. In this case, weak blue emission from the NCO $A^2\Sigma^+ \longrightarrow X^2\Pi$ transition is observed upon photolysis. The time profile of the emission (extending over several μs) indicates that this species is _not_ a direct photoproduct, but rather is formed by a secondary collision process. The apparent second order rate constant for this process, which appears to involve the parent ClNCO, was found to be $7.0 \pm 0.8 \times 10^{-11}$ cm^{3}s^{-1}. Admission of N_2O to the system quenched the NCO $A \longrightarrow X$ emission, and produced instead the well known NO β bands ($B^2\Pi \longrightarrow X^2\Pi$), indicative of the $N(^2D)$ + NO reaction.[6] Hence, it was inferred that $N(^2D)$ was a direct fragment of the photodissociation of ClNCO.

Upon closer examination of the system under a broader range of experimental conditions, a second, longer component to the decay of the blue NCO $A \longrightarrow X$ emission was observed. Admission of NO to the system under conditions where the long decay was observed produced the NO γ bands ($A^2\Sigma^+ \longrightarrow X^2\Pi$) rather than the β bands previously found. These results suggest the action of a second energy carrier capable of reaction with ClNCO to produce NCO(A). The generation of the NO γ bands suggested that the carrier might be $N_2(A^3\Sigma^+)$, a metastable species known to efficiently excite ground state NO to its $A^2\Sigma^+$ state.[7] To test this possibility, ClNCO was added to a flow of $N_2(A)$ metastables generated in a continuous discharge-flow reactor. The interaction of these species did indeed produce NCO $A \longrightarrow X$ emission.

These results (and a number of others obtained during the

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course of the experiments) are consistent with an overall mechanism as follows:

$$ClNCO + h\nu \longrightarrow N(^2D) + Cl + CO \qquad (1)$$

$$N(^2D) + ClNCO \longrightarrow NCl + NCO(A) \qquad (2)$$

$$\longrightarrow N_2(A) + Cl + CO \qquad (2')$$

$$N_2(A) + ClNCO \longrightarrow N_2 + Cl + NCO(A) \qquad (3)$$

$N(^2D)$ is an initial photofragment. It subsequently reacts with ClNCO by either path (2) or (2'), with an overall rate constant 7 X 10^{-11} cm^3s^{-1} as above. The $N_2(A)$ metastables produced in (2') suffer collisions with ClNCO, producing additional NCO(A) as in (5). From the time decay of the slower component of the NCO emission, the rate constant for this process was determined to be k = 2.1 $\pm$ 0.2 X 10^{-11} s^{-1}.

These results suggest that photodissociation of singlet ClNCO($^1A'$) prefers to populate the doublet manifold of fragments, in this case $N(^2D)$ + $Cl(^2P)$ + $CO(X^1\Sigma^+)$. This is in contrast to the case for the analogous halogen azides, which dissociate to singlets (in particular excited singlet NX and singlet ground state N_2) or triplets (ground state NX and excited triplet N_2).[8-10] Singlet or triplet dissociation channels were not observed in the ClNCO experiments. The generality of this result was demonstrated by subsequent experiments with BrNCO and INCO, described below.

A similarity between the halogen azides and ClNCO is that their decomposition (i.e., of the remaining parent) subsequent to

photolysis seems to be carried by intermediates which are electronically excited metastable atoms or molecules. In the present case, these carriers are $N(^2D)$ and $N_2(A)$. This general result suggests that bulk quantities of these energetic species might be stabilized by addition of species which preferentially quench these excited intermediates.

2. Photochemistry of BrNCO and INCO

Photochemical experiments with BrNCO and INCO were performed in a manner identical to those with ClNCO. As shown by Figure 1, two absorption features can be probed in each of these molecules with available excimer laser wavelengths, 193 nm and 308 nm for BrNCO, and 222 nm and 351 nm for INCO. A number of general results were apparent from these experiments.

Photolysis of each molecule in the second absorption feature (λ_{max} = 200 nm for BrNCO and 250 nm for INCO) produced very bright blue NCO A --> X emission, easily visible to the eye in ambient lighting. From the spectrum of the emission, it was apparent that the product NCO(A) was highly vibrationally excited. The quantum yields for production of NCO(A) by photodissociation of BrNCO and INCO at these wavelengths were determined by comparison with the yield of NBr(b --> X) photons produced by photodissociation of similar densities of BrN_3 at 193 nm, a process for which the NBr(b) yield had been previously measured.[9] These experiments indicated the NCO(A) yield from BrNCO photolysis at 193 nm to be 16%, and the yield from INCO photolysis at 222 nm to be 13%. Clearly, production of NCO(A,v) is an important dissociation channel in each case. No evidence for the

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production of NO β or γ bands upon the addition of NO to the system was found. Hence it appears that $N(^2D)$ is not generated as it is in the ClNCO photodissociation described above.

Photolysis of BrNCO and INCO in their first absorption feature, with lasers at 308 and 351 nm, respectively, produced only very weak NCO A --> X emission. This emission was found to vary with the square of the incident laser fluence in each case, indicative of the operation of 2 photon absorption procedures. No NO β or γ emission was found upon the addition of NO, indicating that $N(^2D)$ is not present as a photofragment or intermediate. LIF excitation spectra of the gas medium just after photolysis proved a rich source of information, however. The LIF spectrum for INCO is shown in Figure 2. All of the features found are attributable to transitions in NCO, which are labeled in the Figure. The spectrum indicates that the NCO(X) is not vibrationally excited to any great extent. Further, the intensity of the LIF varies linearly with the incident excimer laser fluence, suggesting that NCO(X) is a direct photofragment. LIF in the visible region produced no evidence of absorption by NBr(X) or NI(X), which should be observed near 674 and 745 nm, respectively, indicating that dissociation to these species is not significant.

From these data and the ClNCO experiments described above, the photochemical processes in ClNCO, BrNCO, and INCO can be summarized as follows:

In the first (longest wavelength) absorption feature:
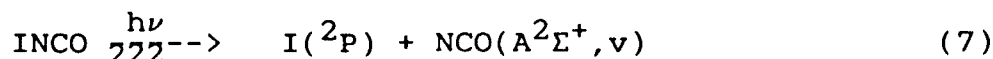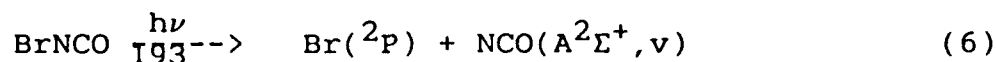
$$\text{ClNCO} \xrightarrow[249]{h\nu} N(^2D) + Cl(^2P) + CO(X^2\Sigma^+) \qquad (1)$$
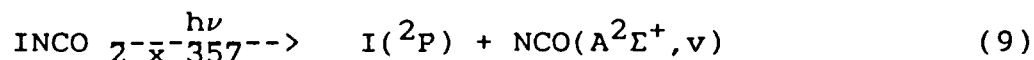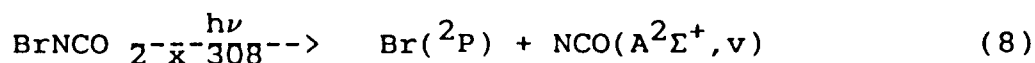
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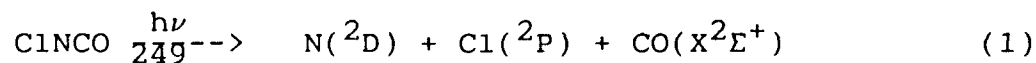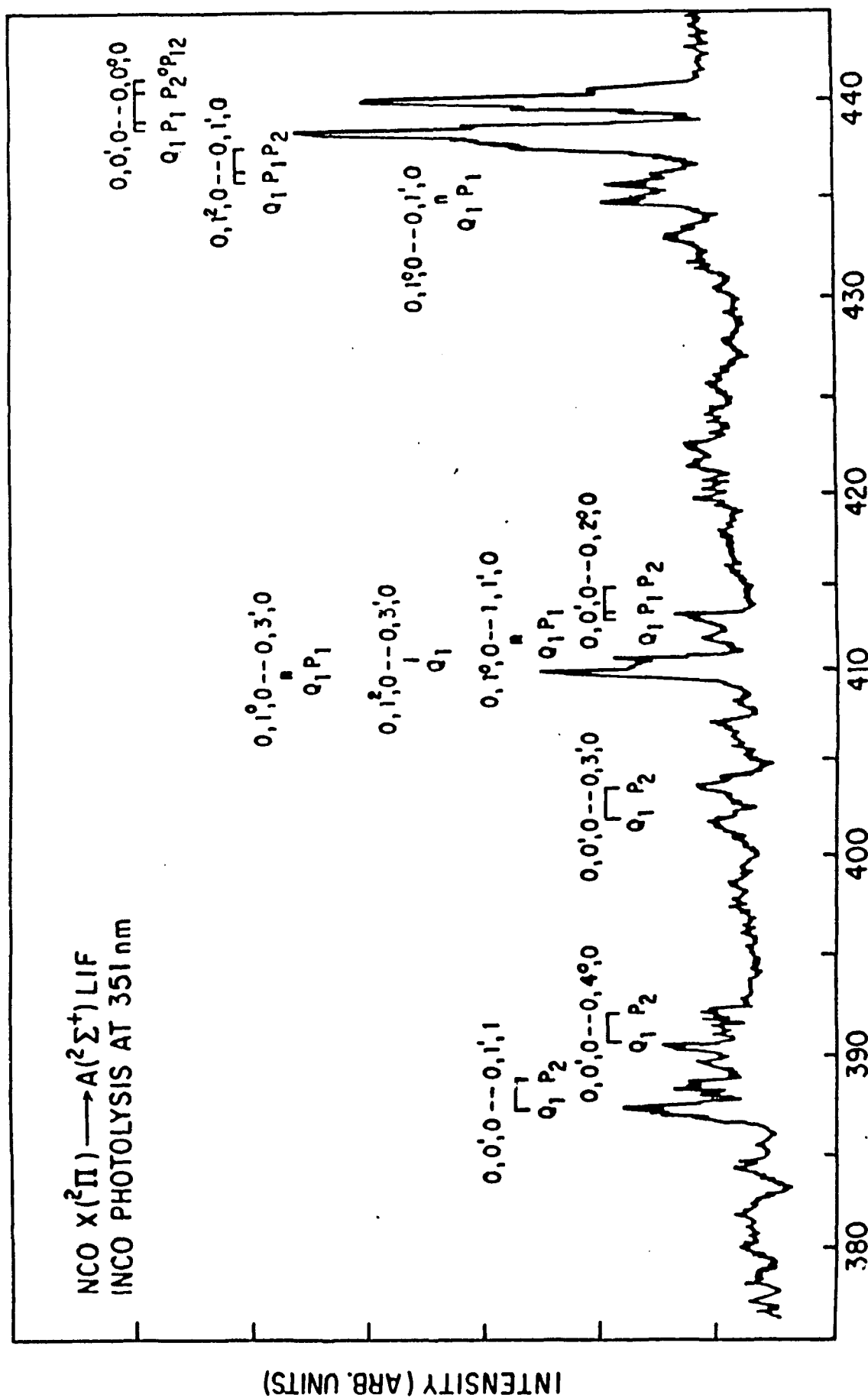
Figure 2. LIF excitation spectrum of NCO ($X^2\Pi$) produced by the photolysis of INCO at 351 nm. $X \rightarrow A$ transitions in NCO are indicated.

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$$\text{BrNCO} \xrightarrow[308]{h\nu} \quad \text{NCO}(X^2\Pi) + \text{Br}(^2P) \tag{4}$$

$$\text{NCO} \xrightarrow[351]{h\nu} \quad \text{NCO}(X^2\Pi) + \text{I}(^2P) \tag{5}$$

In the second absorption feature:

$$\text{BrNCO} \xrightarrow[193]{h\nu} \quad \text{Br}(^2P) + \text{NCO}(A^2\Sigma^+, v) \tag{6}$$

$$\text{INCO} \xrightarrow[222]{h\nu} \quad \text{I}(^2P) + \text{NCO}(A^2\Sigma^+, v) \tag{7}$$
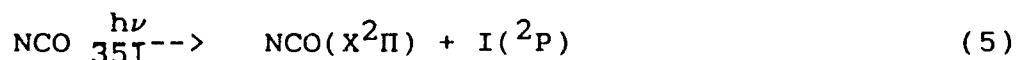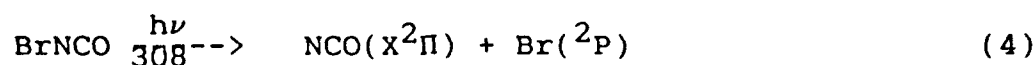
At still shorter wavelengths:

$$\text{BrNCO} \xrightarrow[2-x-308]{h\nu} \quad \text{Br}(^2P) + \text{NCO}(A^2\Sigma^+, v) \tag{8}$$

$$\text{INCO} \xrightarrow[2-x-357]{h\nu} \quad \text{I}(^2P) + \text{NCO}(A^2\Sigma^+, v) \tag{9}$$

In all of the photochemical processes observed the channel leading to the doublet fragments appears to be the major path. In none of the XNCO systems was any evidence of dissociation to triplet or singlet fragments found. This behavior is very different from that in the analogous halogen azides (XN_3),[8-10] and likely reflects the much greater strength of the N-C bond in the halogen isocyanates.

From the nature of excited photofragments produced by one-photon absorptions in these molecules, lower limits for the heats of formation of the parent species can be calculated. These are as follows:

$$\Delta H_f \text{ (ClNCO)} \geq 52 \text{ kcal/mole}$$

$$\Delta H_f \text{ (BrNCO)} \geq 1.7 \text{ kcal/mole}$$

$$\Delta H_f \text{ (INCO)} \geq 10.9 \text{ kcal/mole}$$

Though lower limits, these values are all much greater than ΔH_f for HNCO, reported to be -24.9 kcal/mole.[11] Clearly, these molecules are significantly destabilized by the presence of the halogen atom, likely via repulsive interaction of the filled p atomic orbital of the halogens with the electrons of the delocalized cloud of the NCO chain.

## 3. Photodissociation of NCO($X^2\Pi$) Radicals

The NCO radical is thought to be an important intermediate in the combustion of nitrogenous fuels, and in the generation of NO_x when hydrocarbon fuels are burned in air.[12-14] Direct LIF observation of NCO in the $CH_4/N_2O/N_2$ flame has been reported.[12,13] In addition, NCO has proven to be an important fragment in the dissociation of HNCO and other isocyanates (as above). In spite of the clear significance of this species, only its three lowest lying excited electronic states have been characterized, and little is known about the excited dissociative states which may be involved in reactions or photochemistry.

To address this issue, we performed a series of experiments in which gas phase NCO radicals were photodissociated by light from an ArF excimer laser. LIF methods were used to monitor both the loss of the NCO and the state distribution of the photofragments. This work was based on a 1967 paper by Milligan and Jocex,[15] in which NCO isolated in a low temperature matrix was

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photolyzed at 253 nm, in the predissociative region of the $X^2\Pi \rightarrow B^2\Pi$ transition. Loss of the NCO from the matrix was observed, implying dissociation.

In our experiments, gaseous NCO was produced in a continuous discharge-flow reactor by the reaction of HNCO with fluorine atoms. The density of NCO in the flow was monitored by LIF on the $X^2\Pi \rightarrow A^2\Sigma^+$ transition[16] near 438 nm. In the absence of known absorption spectra, photolysis with several excimer laser wavelengths was tried, with loss of the NCO by photodissociation monitored by diminution of the LIF signals. This diminution was observed only for photolysis at 193 nm, where a reduction of NCO(X) by nearly 5% was observed for an incident fluence near 20 m_J/cm^2, corresponding to an absorption cross section of approximately 5×10^{-20} cm^2 at this wavelength.

Assuming that photolysis of NCO($X^2\Pi$) at 193 nm produces a doublet excited state, two spin allowed dissociation processes are possible:

$$NCO^*(doublet) \begin{cases} N(doublets) + CO(X^1\Sigma^+) & (10a) \\ O(^3P) + CN(doublets) & (10b) \end{cases}$$
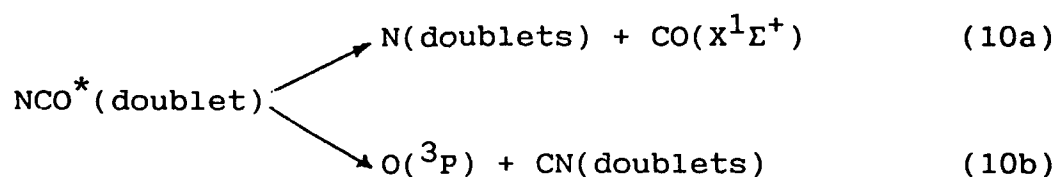
In our experiments, only evidence of the operation of channel (10b) was found, this by LIF on the $X^2\Sigma^+ \rightarrow B^2\Sigma^+$ transition in the product CN. This transition was probed by a tunable dye laser operated near 387 nm which was delayed by a variable time from the photolysis laser pulse. Figure 3a shows an LIF excitation spectrum for a photolysis to probe delay of 0.5 μs. Figure 3b is a simulated CN spectrum for a fitted rotational population
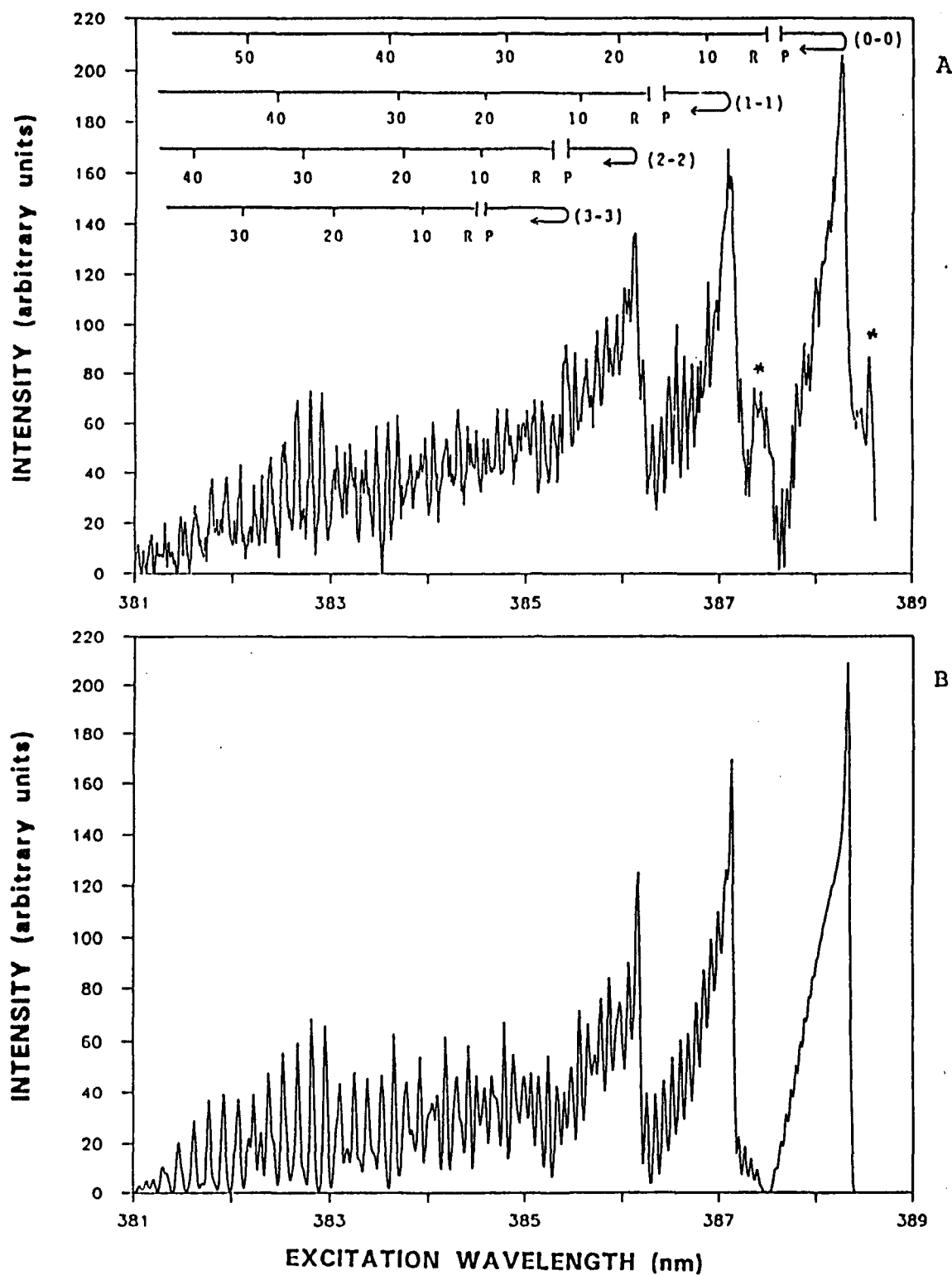
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Figure 3.   A). Experimental LIF excitation spectrum of CN produced by the photodissociation of NCO ($X^2\Pi$) at 193 nm.
B). Calculated spectrum based on known molecular constants, and vibrational/rotational population distributions to give the best fit to the experimental data.

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distribution in the $X^2\Sigma^+$ state (see below). Clearly, the agreement is good. For longer delay times, the CN spectra were well fitted by allowing for relaxation of the initial CN rotational distribution. The CN vibrational distribution was obtained by recording spectra for a delay of 66 μs, when the rotational populations were clearly thermalized, but the vibrational populations should be near nascent.

Figure 4 shows the fitted internal energy distribution in the CN product for short delays corresponding to the LIF spectra of Figure 3. A bimodal distribution is clearly evident. This distribution can be well understood in terms of angular momentum conservation in the dissociation of two excited states, one bent state (which gives rise to the high N portion of the distribution) and one linear state (which gives rise to the low N portion). Details of this discussion are presented in a paper published from this work.[17] Additional evidence for the existence of the linear state was obtained from the spectrum of prompt emission produced by the 193 nm photolysis. This spectrum is shown in Figure 5. The bands observed clearly terminate on vibrational levels of the $A^2\Sigma^+$ state, and the energy of the shortest wavelength band (near 345 nm) corresponds very precisely to the energy difference between a 193 nm photon and the $A(0,0^0,0) \longrightarrow X(0,0^1,0)$ transition, suggesting emission from an excited state pumped at 193 nm to the A state. Further, the observed bands terminate only on stretching modes of the A state (which is linear), suggesting that the upper state is also linear (by Franck-Condon considerations).
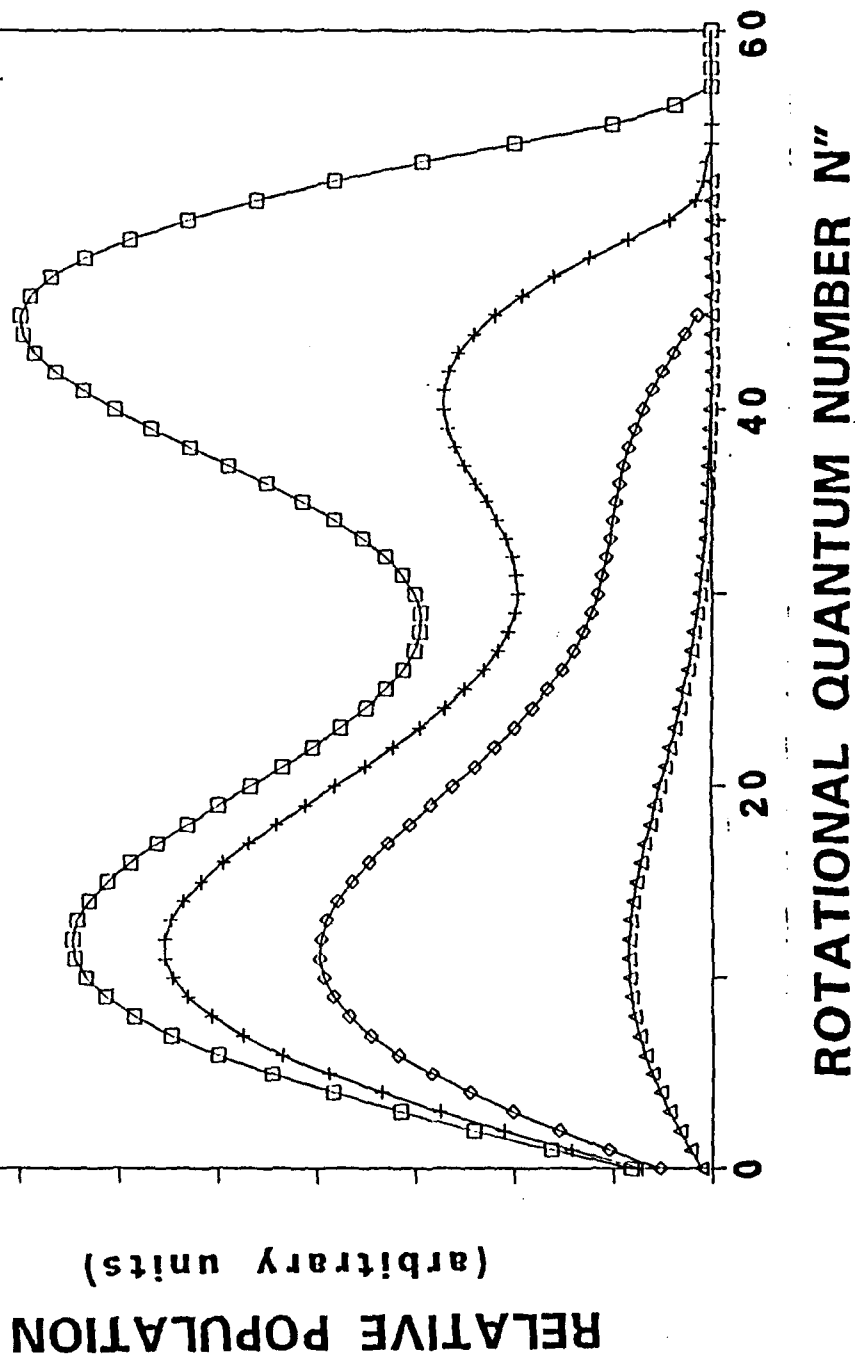
Figure 4. Bi-modal rotational population distributions corresponding to the spectra in Figure 3B. (□), (+), (◇), (△) correspond to rotational distributions for CN(X), v=0, v=1, v=2, and v=3, respectively.

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Figure 5. Spectrum of prompt emission produced by the photolysis of $NCO(X^2\Pi)$ at 193 nm. Transitions are labeled according to the vibrational states of $NCO(A)$ on which they terminate. (*) Indicates second order diffraction of the laser light.

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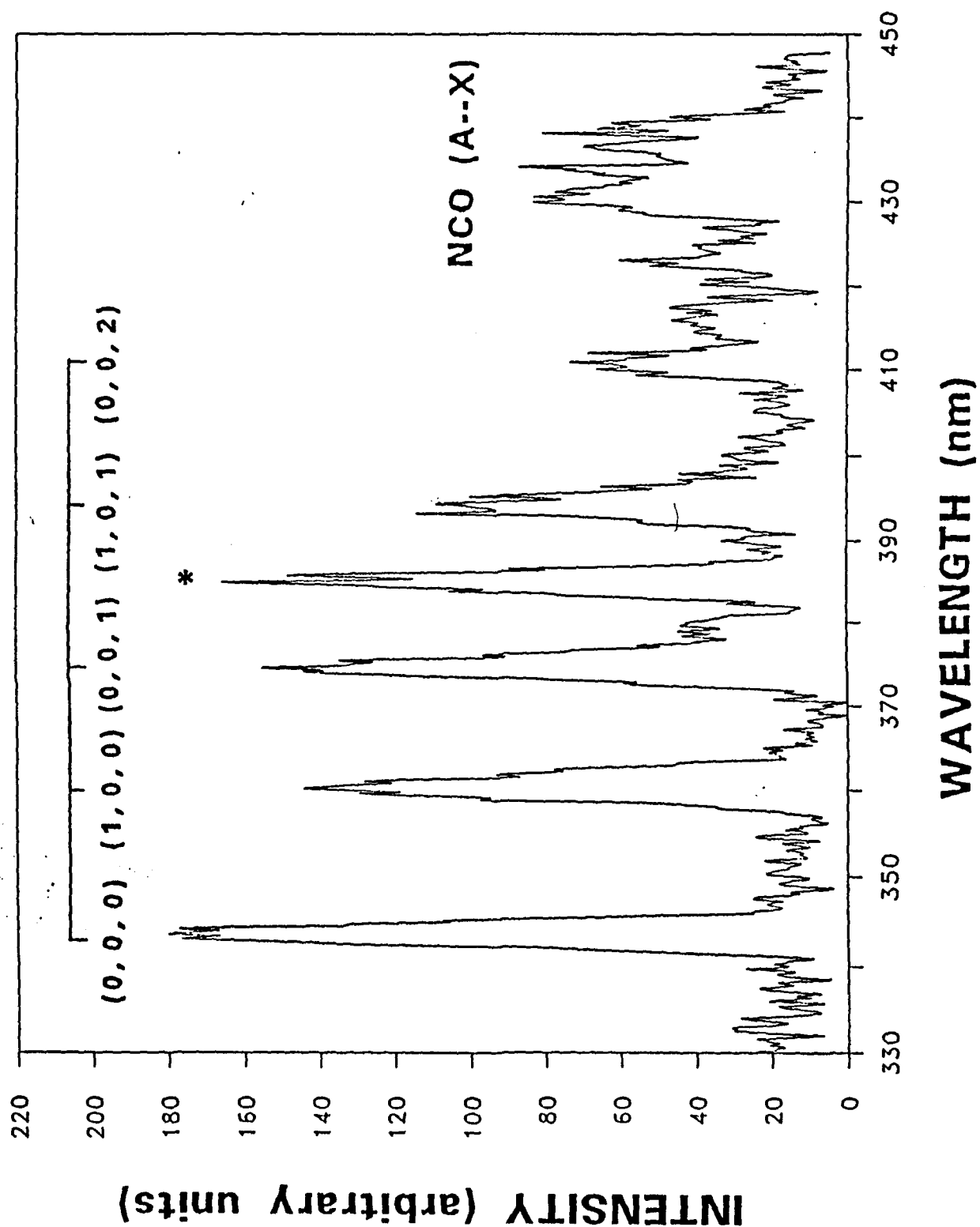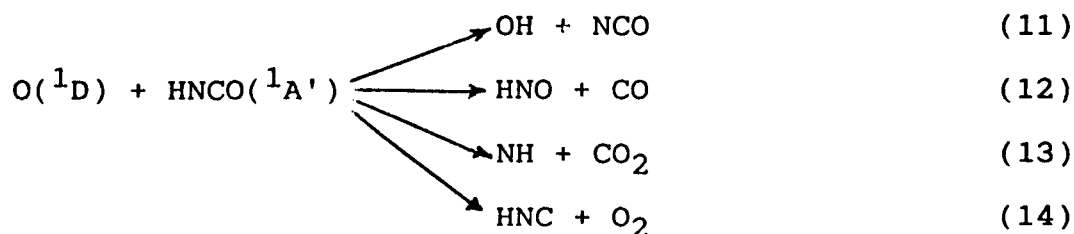Apart from demonstrating the photodissociation of NCO at 193 nm and indicating the existence of a new bound excited state of this radical, these data also serve to give an upper limit on the heat of formation of NCO(X), a value about which there has been considerable debate.[14] From the energy of the 193 nm photon and the maximum internal energy of the CN fragment obtained from the spectral simulation, a limit ΔH_f (NCO) $\geq$ 37 kcal/mole is determined. This result is in very good agreement with that published by Okabe,[18] ΔH_f(NCO) = 36.9 $\pm$ 3.5 kcal/mole, but does not agree well with that reported by Sullivan et. al.,[14] ΔH_f(NCO) > 48 kcal/mole).

4.   Dynamics of the $O(^1D)$ + HNCO Reaction.

As a part of a related program performed in our laboratory, we have recently studied[17] the $O(^1D)$ + HN_3 reaction with the goal of possible improvement of the rates in this system, as well as the yield of $NO(A^2\Sigma^+)$. The NO A --> X transition has been shown to be capable of supporting lasing in the UV region.[20] The $O(^1D)$ + HN_3 reaction was found to proceed in a well-understood manner, the $O(^1D)$ behaving much like $NH(a^1\Delta)$ in its reaction with HN_3, and the desired enhancement in the rates was observed. The analogous $O(^1D)$ + HNCO reaction is a much more interesting case from the perspective of molecular dynamics, since the electrophilic $O(^1D)$ can attack HNCO at each of its four atoms:

$$
O(^1D) + HNCO(^1A') \begin{cases} \longrightarrow OH + NCO & (11) \\ \longrightarrow HNO + CO & (12) \\ \longrightarrow NH + CO_2 & (13) \\ \longrightarrow HNC + O_2 & (14) \end{cases}
$$

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To test these possibilities, numerous experiments were performed in our laboratory in which the $O(^1D)$ + HNCO reaction was initiated by pulsed photolysis of premixed, flowing streams of O_3 and HNCO with a KrF excimer laser at 249 nm. The products of the reaction were probed by emission and LIF methods.

No evidence was found for the occurrence of any reactions other than processes (11) and (13) above, with (13) being clearly dominant. The only chemiluminescence produced by the reaction is NH $A^3\Pi$ --> $X^3\Sigma^-$ emission near 336 nm. From the time decay of this emission, the overall rate constant for the reaction was determined to be $3.3 \pm 0.3 \times 10^{-10}$ cm^3s^{-1}, nearly the gas kinetic value. $NH(X^3\Sigma^-)$, $NH(a^1\Delta)$, NH $(b^1\Sigma^+)$, and $NCO(X^2\Pi)$ were monitored by LIF methods. LIF excitation spectra were recorded for $NH(a^1\Delta)$, $NH(X^3\Sigma^-)$, and $NCO(X^2\Pi)$, but no evidence of $NH(b^1\Sigma^+)$ was found.

Figure 6 shows time profiles of the LIF signals from NH(a), NH(X) and NCO(X). The NH(a) profile shows a risetime which agrees with the rate of the $O(^1D)$ + HNCO reaction, and a decay which matches the rate of the subsequent NH(a) + HNCO reaction. Hence this profile suggests that NH(a) is a direct product of the reaction. In contrast, the time profiles of NH(X) and NCO(X) show a much slower rise to a plateau, consistent with formation by secondary reactions. The dotted and broken curves shown in these figures are calculated time profiles corresponding to direct production of these species by the $O(^1D)$ + HNCO reaction or production by secondary reactions, respectively. The data contain information about the relative importance of these two routes, which may be quantified if the absolute yield of $NH(a^1\Delta)$ is

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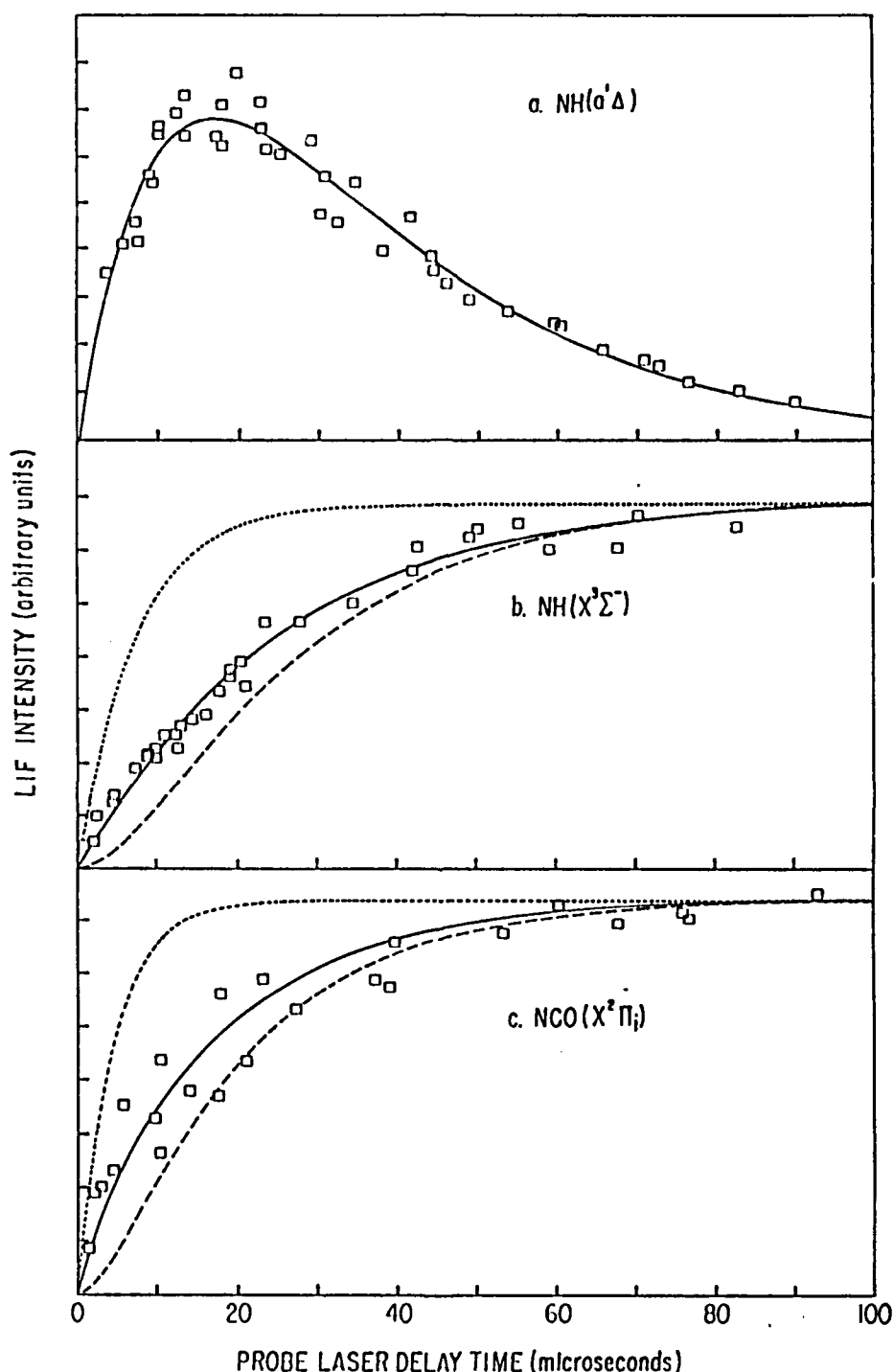
Figure 6. Time profiles of (a) NH (a$^1\Delta$), (b) NH (X$^3\Sigma^-$), and
(c) NCO (X$^2\Pi$) obtained from changes in the corresponding
LIF intensities with probe laser delay time. Dotted
curves in (b) and (c) are calculated time profiles based
on mechanisms in which NH(X) and NCO(X), respectively,
are produced by the primary O(^{1}D) + HNCO reaction only.
Broken curves are calculated time profiles based on
mechanisms in which NH(X) and NCO(X) are produced only
by a secondary NH(a) + HNCO reaction.

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known. Details of this treatment are presented in a manuscript[21] submitted for publication in the Journal of Physical Chemistry. The absolute yield of NH(a) was determined by comparison of the LIF intensity observed for this species with that for NH(a) produced by photodissociation of HN_3 at 193 nm.[22] These experiments indicated that the $O(^1D)$ + HNCO branching fraction to $NH(a^1\Delta, v=0)$ is 44 ± 15%. This result, in combination with the temporal data in Figure 6, indicates that the <u>maximum</u> branching fractions to NH(X) and NCO(X) in this reaction are 16% and 20%, respectively. From additional absolute yield measurements, the branching fraction to $NH(A^3\Pi)$ was found to be < 0.02%.

Clearly, the $O(^1D)$ + HNCO reaction has a strong propensity for production of $NH(a^1\Delta)$. This can be understood in part by conservation of spin angular momentum, in which the singlet potential energy surface corresponding to $O(^1D)$ + $HNCO(^1A')$ correlates adiabatically to $NH(a^1\Delta)$ + $CO(X^1\Sigma^+)$. The reactants also correlate to $NH(b^1\Sigma^+)$ + $CO(X^1\Sigma^+)$, however, and <u>no</u> NH(b) was found in the experiments. Hence, orbital symmetry correlations must also play a role. In any event, this reaction is a very rapid, very efficient source of $NH(a^1\Delta)$ metastables, produced in combination with $O_2(a^1\Delta)$ metastables which are a co-product of the O_3 photodissociation. Given the speed of the reaction, which is much faster than the known rates[23] of $NH(a^1\Delta)$ quenching by residual HNCO, this system may provide a scalable, quite useful source of metastable energy carriers for chemical laser applications.

III. HALOGEN AMINE CHEMISTRY

1.   Synthesis of Fluorochloroamines

As will be discussed below, fully halogenated amines are very interesting energetic molecules, which can act as sources of electroncially excited singlet halogen nitrenes (NX) by either reactions or photochemistry. In order to pursue our interest in these compounds, procedures for their synthesis and purification were modified and optimized in order to yield useful amounts of relatively pure samples. The particular species studied to date are NCl_3, $NFCl_2$, and NF_2Cl.

The synthesis developed for $NFCl_2$ and NF_2Cl is a modification of that originally reported by Pankratov and Sokolov,[24] and involves the fluorination of NH_4Cl with elemental F_2 in a flow reactor. In our study, it was found that the addition of NaCl to the NH_4Cl significantly increased the yields of the desired fluorochloramines. Careful drying of the reaction system is important to avoid the formation of $FClO_3$ and $FONO_2$. Although the yields of $NFCl_2$ and NF_2Cl are relatively low, and separation of the main by-product Cl_2 requires careful fractionation, the method is a relatively convenient and safe way to produce moderate amounts of $NFCl_2$ and NF_2Cl. It avoids the hazards associated with the formation of chlorine azide as a potential by-product in the chlorofluorination of NaN_3.

Our synthesis for NCl_3 mirrors that used by a number of previous researchers,[25] the major improvements being largely a matter of technique.

2. Photochemistry of $NFCl_2$ and NF_2Cl in Low-Temperature Argon Matrices

Only a few brief reports have appeared in the literature concerning the photolysis of the fluorochloroamines ($NFCl_2$ and NF_2Cl).[26-28] These experiments, done largely in the 1960's, involved the gas-phase amines and used broad-band photolysis sources. The data strongly suggested that various NX_2, NXY, and NX compounds (X,Y = halogens) could be photolytically produced from the fluorochloroamines, although no direct evidence of these intermediates was obtained. In order to study the photochemical processes in detail, we have isolated and photolyzed the fluoro-chloroamines in low-temperature argon matrices, and identified the photoproducts via IR spectra of the matrices. The photolysis energies were chosen on the bais of the UV absorption spectra of the gas phase amines obtained in our laboratory. Each spectrum consists of a single broad structureless feature at 270 nm for $NFCl_2$ and at 230 nm for NF_2Cl.
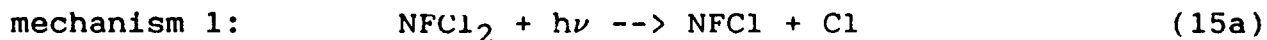
Infrared spectra were used to monitor the results of the photolysis experiments. Broadband photolysis of the NFCl/Ar matrix produced a sharp peak at 1113 cm^{-1}, two weaker features at 742 and 870 cm^{-1}, and the intensity of the $NFCl_2$ peaks decreased during the photolysis. In addition, a peak appeared at 821 cm^{-1}, on the shoulder of ν_5 (the NF stretch of $NFCl_2$). Photolysis of the $NFCl_2$/Ar matrix at 270, 250 and 300 nm produced an infrared absorption at 1113 cm^{-1}, the accompanying decrease of the $NFCl_2$ infrared absorption peaks, and absorbences at 742 and 870 cm^{-1}. The 1113 cm^{-1} peak was assigned to NF and is consistent with the
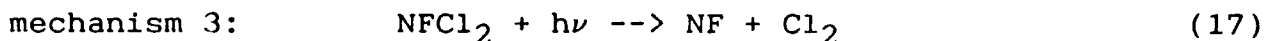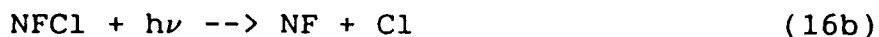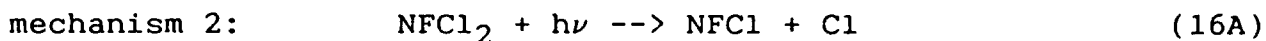
assignment made by Milligan and Jacox[29] in which NF was produced from the photolysis of FN_3 in a low temperature matrix. The absorbences at 742 and 880 cm^{-1} have not been identified, but are not due to cis-N_2F_2. (This compound has three absorption peaks at 737, 896 and 952 cm^{-1}.[7]) A peak at 824 cm^{-1} was assigned to NCl in the NCl_3/Ar matrix photolysis experiments and the 821 cm^{-1} absorbance could be due to NCl in these experiments.

In the single wavelength experiments, the rate of increase of the NF integrated intensity was substantially larger at 270 nm, the maximum in the UV absorption, than at 250 nm or 300 nm. Photolysis of the $NFCl_2$/Ar matrix at 210 nm and at 330 nm produced no change in the IR spectrum.

From the production of NF observed in the single wavelength photolysis experiments of $NFCl_2$, it is apparent that the 270 nm absorption feature in the UV spectrum does indeed lead to an unbound state of the molecule. Since no changes were observed after photolysis at 330 nm, then any Cl atoms produced (due to the presence of Cl_2, a byproduct of the synthesis) did not interact with the $NFCl_2$.

The products generated by photolysis of the matrix are "locked" in matrix cages, Cl atoms are apparently too large to escape, and hence the possible mechanisms by which NF can be formed in these experiments are limited. The following three mechanisms are proposed.

mechanism 1: $NFCl_2 + h\nu \longrightarrow NFCl + Cl$ (15a)

                           $NFCl + Cl \longrightarrow NF + Cl_2$ (15b)

mechanism 2: $NFCl_2 + h\nu \longrightarrow NFCl + Cl$ (16A)

$NFCl + h\nu \longrightarrow NF + Cl$ (16b)

mechanism 3: $NFCl_2 + h\nu \longrightarrow NF + Cl_2$ (17)

Based on the results obtained to date, mechanism 1 appears to be the most unlikely of the three. It would require motion in the cage in order for the first Cl to align itself so as to react with the NFCl fragment to produce Cl_2 + NF. Motion within the cage is very restricted. Mechanism 2 requires that both $NFCl_2$ and NFCl absorb at the same wavelength, and that as soon as the NFCl is formed it is photolyzed efficiently at this wavelength (no evidence of the production of NFCl is observed in the IR spectrum). NFCl has never been isolated and studied so its spectroscopy is completely unknown. Mechanism 3, a concerted process in which one photon is absorbed and both N-Cl bonds are broken simultaneously leaving NF, appears to be the most reasonable choice at this point. Whatever the mechanism, however, it is clear that NF is produced from the photolysis of $NFCl_2$ and that the absorption at 270 nm in the $NFCl_2$ UV spectrum leads to its formation.

Photolysis of the NF_2Cl/Ar matrix did not produce any changes in the IR spectrum, but this does not necessarily mean that no photolysis was taking place. On the contrary, the fact that a structureless peak is observed at 230 nm in the UV spectrum does indeed imply dissociation. After careful consideration of our data and of the early NF_2Cl studies mentioned above, we believe that the process taking place in the matrix is cleavage

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of the N-Cl bond leaving NF_2 and Cl in the matrix cage which recombine to form the parent amine.

3.   Production of Excited Singlet NCl by the Reaction of NCl_3 with Hydrogen Atoms

The production of excited singlet NF by the reaction of hydrogen atoms with NF_2 has been studied in many previous experiments.[30] Such processes are of interest because of the very strong dynamic constraints on the distribution of product states, and because $NF(a^1\Delta)$ has potential utility as an energy carrier in high energy laser systems. The branching fraction to NF(a) in the H + NF_2 reaction has been determined[31] to be 0.91. The product state selectivity in this case is thought to arise from an addition-elimination mechanism involving attack by the hydrogen atom on the nitrogen atom of NF_2 to produce an excited singlet difluoramine intermediate, which eliminates singlet HF to leave excited singlet NF. This process has been used[32] to generate NF(a) densities in excess of 10^{15} cm^{-3}. In principle, similar reactions of H atoms with other NX_2 or NXY radicals (X,Y = halogen) might also produce high yields of excited singlet NX species. Such reactions have not been explored, however, in large measure because chlorinated or brominated analogues of N_2F_4 (the normal precursor of NF_2) are unknown.

Like N_2F_4, fully halogenated amines NX_3 or NX_2Y can be used as precursors of NX_2 or NXY radicals, and hence of excited nitrenes by reactions with H atoms. In this project, these ideas were tested by observing the reaction of NCl_3 with excess H atoms in a continuous discharge-flow reactor. Excited NCl can be pro-

duced in this system by a two step mechanism as follows

$$H + NCl_3 \longrightarrow HCl + NCl_2 \qquad (18)$$

$$H + NCl_2 \longrightarrow HCl + NCl^* \qquad (19)$$
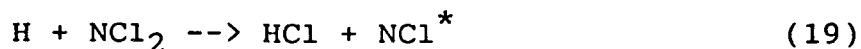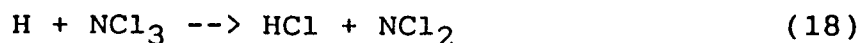
To the extent that reaction (19) proceeds via the addition-elimi-nation mechanism, excited singlet NCl should be produced.

Hydrogen atoms were produced by reaction of a titrated flow of F atoms with H_2. NCl_3 heavily diluted in Ar was admitted upstream via a movable injector. The subsequent reaction produced a bright red flame clearly visible to the eye. Figure 7a shows a spectrum of the visible emission, which is identified as the NCl $b^1\Sigma^+$ transition. Figure 7b shows the spectrum of the chemiluminescence in the near IR, indicating the $a^1\Delta \longrightarrow X^3\Sigma^-$ transition in NCl. Under carefully controlled conditions, it can be shown[33] that the time dependence of the NCl b $\longrightarrow$ X emission will track the density of the intermediate NCl_2, and should exhibit an exponential rise and decay controlled by the rates of processes (18 and (19). This was found to be the case, and the rate constants determined were $9 \pm 4 \times 10^{-11}$ cm^3s^{-1} and $4.0 \pm 0.4 \times 10^{-12}$ cm^3s^{-1}. A priori, we cannot know which rate constant applies to which reaction. Since the rate constant for H + NF_2 is much larger than that for H + NF_3,[30] and it seems reasonable that a similar relationship should hold for the NCl_3 system, our best guess is that $k = 4.0 \pm 0.4 \times 10^{-12}$ cm^3s^{-1} applies to reaction (18).
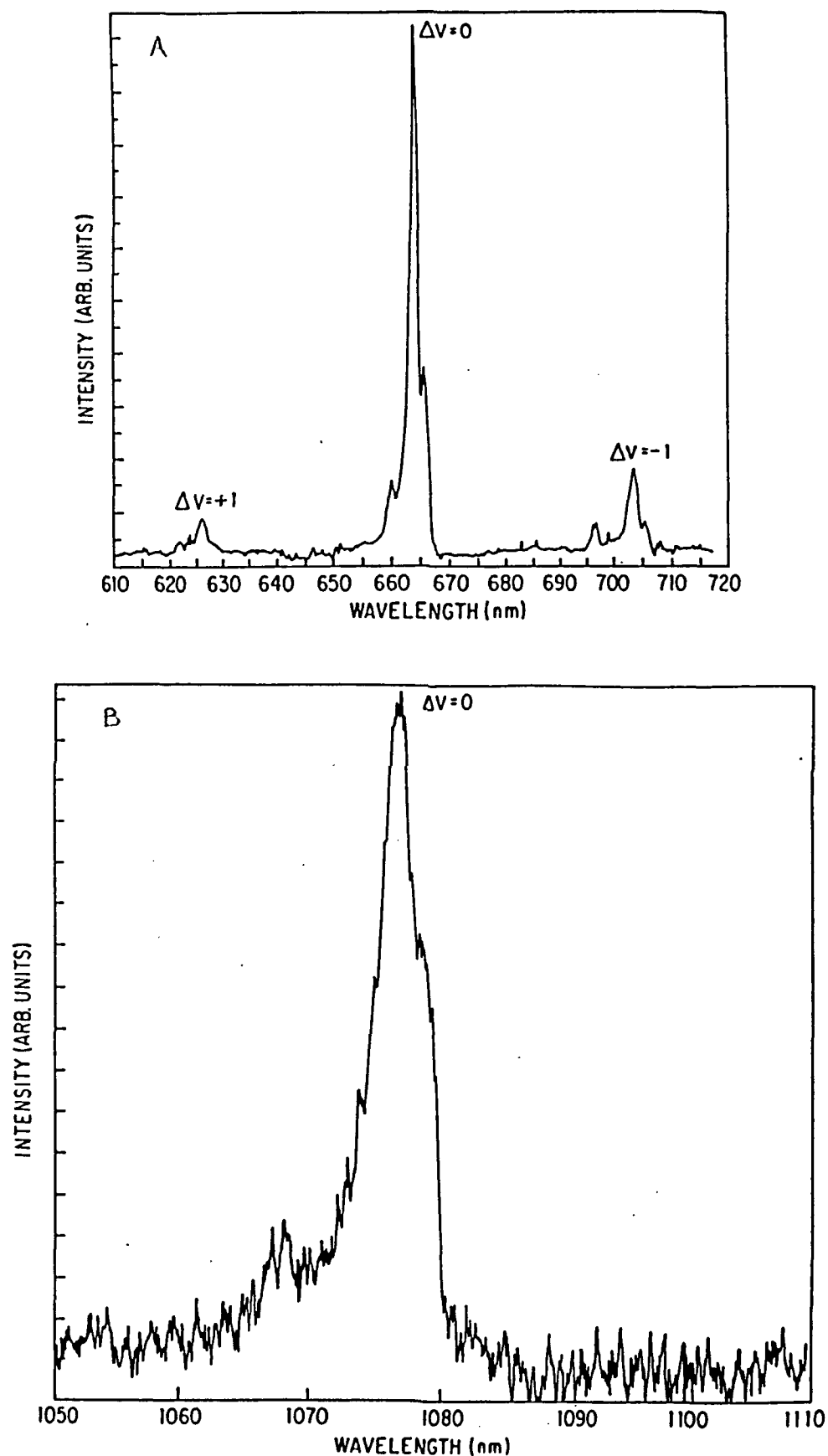
Figure 7. Spectra of Chemiluminescence from the H + NCl_3 system. (A). The NCl $b^1\Sigma^+ \to X^3\Sigma^-$ transition; (B), the NCl $a^1\Delta \to X^3\Sigma^-$ transition.

Photon yields for the NCl b --> X and a --> X chemiluminescence were measured by calibration of the detection apparatus with the well known $O + NO --> NO_2 + h\nu$ reaction. The yields were determined as the ratios of the rate of flow of NCl(b) or NCl(a) photons from the system vs. the flow of NCl_3 into the reactor. The NCl(a) photon flow was corrected for the fraction of the excited molecules that actually radiate (relative to quenching in collisions with other species or with the reactor walls), determined from the observed time decay of the emission and the radiative rate of the transition.[34] The measurements of the yields were such that the results must be taken to reflect only lower limits on the actual branching fractions for reaction (19). From the data, the branching fraction to NCl ($a^1\Delta$) has a lower limit of 15%. The branching fraction to NCl (b) is very small, with a lower limit of 0.015%, approximately three orders of magnitude smaller than the NCl a --> X yield.

From these experiments, it is clear that reactions of halogen amines with H atoms can be useful sources of excited metastable halogen nitrenes. NCl_3 is itself an unstable and shock sensitive species (in its condensed state). It would seem the $NFCl_2$ and NF_2Cl, much more stable molecules, are superior candidates for real applications. We are currently studying H atom reactions with these species.

IV. COLLISIONAL DISSOCIATION OF HALOGEN AZIDES

Benard and co-workers[34,35] have shown that the halogen azides FN_3 and ClN_3 can be thermally dissociated to give high yields of $NF(a^1\Delta)$ and $NCl(a^1\Delta)$ fragments, respectively. These weakly bound molecules exist in shallow wells on the ground state $^1A'$ potential energy surface. Excitation sufficient to overcome the barriers that bind these molecules leads to dissociation to adiabatically correlated singlet fragments (e.g., NF $a^1\Delta$ + N_2 $X^1\Sigma_g^+$), with the release of substantial amounts of energy. These processes have been shown to be an effective source of high densities of the excited nitrenes, and are applicable to the development of high energy laser technology. They are also particularly interesting with respect to the fundamental dynamics of dissociation processes, however. As very weakly bound (~10 kcal/mole) molecules with potential energy wells that are likely to be very anharmonic, these species present a very interesting test of statistical theories of unimolecular decomposition, and interesting possibilities for mode specific excitation and dissociation.

A particular case in point is energy transfer between vibrationally excited HF and halogen azide molecules. The frequencies of the symmetric and asymmetric stretches along the N_3 chain are near 2000 cm^{-1} and 1000 cm^{-1}, respectively, for most RN_3 species.[36] Since the HF frequency is near 4000 cm^{-1}, good possibility exists for fast resonant energy exchange. Because the projections of these vibrations on the $RN-N_2$ dissociation coordinate

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are very large, excitation of these vibrations at energies above the barrier could lead to rapid dissociation before randomization of the energy among other degrees of freedom of the molecule.

We have performed initial tests of these ideas by observing $HF(v)$ - RN_3 (R = H, Cl, Br) energy transfer processes using both pulsed and continuous methods. The first experiments involved chemical generation of vibrationally excited HF in a flow reactor by the F + H_2 reaction, followed by admission of ClN_3 or BrN_3 downstream. In both cases, visible chemiluminescence from $NCl(b^1\Sigma^+)$ or $NBr(b^1\Sigma^+)$ respectively, was produced, indicating dissociation of the parent halogen azide. The conditions of the experiments (< 1 Torr total pressure, with reagent densities on the order of tens of mTorr) were such that any temperature rise in the system could not possibly be such as to cause the dissociation. To test the role of $HF(v)$ in the systems, CO_2 was added to selectively quench this species. CO_2 is an efficient quencher of $HF(v)$, but an inefficient quencher of $NCl(b)$.[37] Admission of CO_2 quenched the $NCl(b)$ emission from ClN_3 and the $NBr(b)$ emission from BrN_3, suggesting that dissociation of the parent molecules is indeed caused by energy transfer from $HF(v)$.

Following these initial qualitative experiments, an apparatus for pulsed energy transfer experiments was assembled in order to gather more quantitative data. These tests involved pulsed photolysis of HF/XN_3/diluent mixtures with an IR laser operating on HF vibrational transitions. Overall energy transfer rates were determined by the quenching of infrared LIF from the HF as a function of the azide concentration. For $HF(v=1)$ quenching by HN_3 and ClN_3, these experiments yielded k = 3 X 10^{-11} cm^3s^{-1} and

$k = 3 \times 10^{-12}$ cm^3s^{-1} respectively. These values are reasonable for fast V-V energy transfer processes. A second part of the experiments involved looking for infrared and visible chemilumescence from the azides or their nitrene fragments. Work on this aspect of the project is still ongoing. Preliminary results, however, had added support to the proposed V-V mechanism,. In particular, IR emission near 5.0 μm (in the region of the N_3 asymmetric stretch) has been observed from HN_3 subsequent to photolysis of the HF/HN_3 mixture with the HF laser. This is reasonable in this case, since the energy transferred is insufficient to dissociate the molecule. NCl emission has not yet been observed in preliminary experiments with the HF/ClN_3 system.

We intend to proceed with these experiments under the auspices of our continuing AFOSR grant. Eventually, this project will evolve into experiments in which metastable XN_3 species are dissociated by collisions at carefully defined energies in a molecular beam apparatus.

V.   PUBLICATIONS ARISING FROM THIS PROGRAM

1.   J.V. Gilbert and R.D. Coombe, "Photochemistry of ClCNO," J. Chem. Phys., $\underline{89}$, 4082 (1988).

2.   X. Liu, J.V. Gilbert, and R.D. Coombe, "Photochemistry of BrNCO and INCO," J. Chem. Phys., $\underline{90}$, 171 (1989).

3.   X. Liu and R.D. Coombe, Photodissociation of $NCO(X^2\Pi)$ Radicals," J. Chem Phys., $\underline{91}$, 7543 (1989).

4.   J.V. Gilbert, R.A. Conklin, R.D. Wilson, and K.O. Christi, "Syntheses and Vibrational Spectra of Chlorofluoramines," J. Fluorine Chemistry, $\underline{48}$, 361 (1990).

5.   R.A. Conklin and J.V. Gilbert, "Photochemistry of Fluorochloroamines in Low Temperature Argon Matrices," J. Phys. Chem., $\underline{94}$, 3027 (1990).

6.   X. Liu, N.P. Machara, and R.D. Coombe, "Dynamics of the $O(^1D)$ + HNCO Reaction," submitted to J. Phys. Chem., 1990.

7.   D.B. Exton, J.V. Gilbert, and R.D. Coombe, "Generation of Excited NCl by the Reaction of Hydrogen Atoms with NCl_3," submitted to J. Phys. Chem., 1990.

VI. PERSONNEL

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[*]Ph.D. awarded, August 1989
[**]M.S. awarded, August 1989

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